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THE RADIOCHEMICAL CHARACTERIZATION OF NPD CONCRETE CORE SECTIONS

Report No. 90-285-K

J.P. Krasznai
Research Scientist
Materials Chemistry Section
Chemical Research Department

ABSTRACT

The shutdown of the Nuclear Power Demonstration (NPD) reactor in 1987 after 25 years of operation provided an opportunity to sample concrete subjected to neutron and gamma irradiation over this period and study its physical, chemical and radiochemical composition. Such characterization provides important information on not only the effects of neutron exposure on the physical properties of concrete, but also to answer questions related to the management of decommissioning waste, concrete decontamination as well as the behavior of radionuclides in cement based engineered barriers. The inventory and distribution of radionuclides have been determined and the rate of desorption of tritiated water from regular and high density concrete was measured.

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EXECUTIVE SUMMARY

THE RADIOCHEMICAL CHARACTERIZATION OF NPD CONCRETE CORE SECTIONS

J.P. Krasznai

After 25 years of operation, the Nuclear Power Demonstration (NPD) reactor was shutdown in 1987. The decommissioning of NPD provided opportunities for scientific investigations relevant to Ontario Hydro's aim to ensure continued safe operation of nuclear plants beyond their 40 year design life.

Primarily because of its use in reactor structures, concrete was classified as a critical component and a number of concrete core sections made from regular and high density concrete were removed from various locations in early 1988. Concrete is used extensively in nuclear plants and associated facilities as:

(a) a containment boundary and biological shield,

(b) in nuclear waste repositories as engineered structural and backfill material,

(c) containers for irradiated fuel and other radioactive waste,

(d) solidification matrix for low and intermediate level radioactive waste.

In view of the extensive use of concrete in nuclear facilities, the R&D program objectives relating to NPD cores were expanded to not only determine age and service related degradation effects in regular and high density concrete in nuclear service, but also to determine the radionuclide content and activity distribution in the various types of concrete exposed to radiation and contamination. These data would provide valuable information on:

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(a) the options available for the dismantling of concrete structures during the second phase of decommissioning ie 30 years post closure.

(b) the degree of radionuclide retardation provided by engineered concrete structures and cementitious backfill materials used in the construction of low and intermediate level radioactive waste disposal facilities.

(c) the behaviour of tritium contamination in concrete structures associated with fusion reactor facilities.

This report describes a radiochemical characterization of the concrete cores removed from the shielding wall between the boiler room and the reactor vault as well as the wall forming the moderator dump tank sump. The contact radiation field associated with the reactor vault end of the core removed from the boiler room shielding wall was over 100 mR/h due predominantly to neutron activation of cobalt impurity in the high density concrete. Other isotopes identified by gamma spectrometry included Mn-54, Cs-134/137, Eu-152/154 and Ce-144. The activity of Co-60 (1770Bq/g) in the cement at the vault end of the cores was two hundred times greater than at the boiler room end due to the rapid attenuation of neutrons in high density concrete. The same trend was apparent for the other gamma emitting isotopes.

The specific activity of Fe-55, a low energy X-ray emitter was not determined directly due to the difficulty of the analysis but its calculated maximum concentration is 323kBq/g which would make it the most abundant radioisotope in the high density concrete. However its low energy radiation and its relatively short half life (2.6y) makes Fe-55 a relatively unimportant isotope with respect to Phase II decommissioning and subsequent waste management strategies.

A protocol to determine the concentration of the hard to measure beta emitters Ni-63 and Ca-41 was developed by Analytical Services. The Ni-63 and Ca-41 content were 3 and <1 Bq/g respectively which for the Ni-63 isotope is a factor of 30 less than calculated probably due to errors associated with applying the complex analytical protocol to a relatively small sample.

The C-14 analyses of the vault/boiler room core section showed that C-14 concentrates at the concrete surface with the boiler room end of the core (296 Bq/g) being 4 times the concentration of the vault end (67Bq/g). The activity decreased to background levels (4Bq/g) within 0.5 cm of the surfaces. A greater concentration at the vault end was expected because of exposure of the concrete to vault air containing $^{14}CO_2$ formed by neutron activation of nitrogen in air. However a mild steel liner covered the inside of the vault walls effectively protecting the concrete from carbonation from $^{14}CO_2$.

The lower concentration of tritium at the vault end (300-500 Bq/g) relative to the boiler room end is also attributed to the protective steel plate preventing water vapour access to the concrete. There is a maximum tritium activity of 12-15 kBq/g concrete which occurs approximately 5 cm from the boiler room end of each core. This is attributable to the core sampling process which would have washed tritium from the surface and just below. The total tritium in the core section from the vault/boiler room is calculated to be 107.4MBq (2.9mCi). By comparison, the maximum tritium concentration and total inventory in the core section removed from the moderator dump tank wall constructed of regular density concrete was 82kBq/g cement and 290MBq (8mCi) respectively.

The rate of desorption of tritium from both regular and high density concrete is 5.0×10^{-3} cm.day^{-1} and 1.5×10^{-3}cm.day^{-1} respectively. The desorption process is diffusion controlled as evidenced by the ability to fit the tritium desorption behaviour to a semi-infinite plane source diffusion model based on mass transport theory. The effective tritiated diffusivity, D_e, calculated for high and regular density concrete is 5.2×10^{-9} cm^2.s^{-1} and 6.6×10^{-8} cm^2.s^{-1} respectively and agrees with data from the literature. The diffusivity for both types of concrete is 4 orders of magnitude lower than the self diffusion coefficient of tritiated water in light water.

The information generated in this report will provide a guide in the development of decontamination and waste management strategies when planning Phase II decommissioning. For example at the end of the 30 year Phase I of decommissioning, the activity of the concrete from NPD will be dominated by tritium. Decontamination of the concrete could be accomplished by establishing an air purge through the NPD boiler room a few years before Phase II decommissioning begins. This would result in a large volume of radioactive waste that could be declared de minimis or below regulatory concern after decontamination. In addition the tritium diffusion data allows an assessment of the radiation hazards due to tritium and the mitigating techniques required to protect workers during Phase II decommissioning activities.

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To: Dr. D. Mills
Director of Research

THE RADIOCHEMICAL CHARACTERIZATION OF NPD CONCRETE CORE SECTIONS

J.P. Krasznai

1.0 INTRODUCTION

After 25 years of operation, the Nuclear Power Demonstration (NPD) reactor was shutdown in 1987. During its lifetime the station was successfully used to demonstrate CANDU concepts and for staff training and development. Plans for the decommissioning of NPD are similar to Gentilly I and the Douglas Point nuclear plants which are following three internationally accepted phases:

Phase I: The station is shut down, the heavy water and fuel are removed from the reactor and all fuel is transferred to dry storage.

Phase II: The station is placed in the *Storage With Disposal* mode for a period of 30 years.

Phase III: All systems and structures are completely dismantled.

Following shutdown, Phase I of decommissioning was completed when the reactor was defueled and all nuclear systems were drained and dried.

The decommissioning of NPD provided a number of opportunities for scientific investigations relevant to Ontario Hydro's aim to ensure continued safe operation of nuclear plants beyond their 40 year design life/1/. Specimens of critical plant components were removed to study age related degradation mechanisms in an attempt to anticipate and rectify such deterioration of similar components in mature operating plants. It is hoped that this will assure reliable and safe plant operation during the design life of the plant, and provide the economic basis for extending the operation of these plants beyond their design lifetimes.

This is the basic objective of the Nuclear Plant Life Assurance (NPLA) Program. The proposed R&D work in support of the NPLA program is detailed in reference 2.

TABLE 1

LOCATION OF CONCRETE CORES REMOVED FROM NPD

Location ID	Location	Concrete Type	Temperature	Radiation
1	Boiler Support Beam	Special	High	Gamma & H-3
2	Boiler Room to Reactor Vault	High	High	Gamma, H-3 Neutron
3	Dump Tank Room To Soil	Regular	Moderate	H-3
4	Boiler Room to Condenser Room	Regular	High	Gamma & H-3
5	Boiler Room to Soil	Regular	High	Gamma & H-3
6	Decon. Room to Reactor Vault Cooling Room	Regular	Moderate	H-3
7	Reactor Vault Cooling Room to FM Room	Regular	Moderate	H-3
8	Boiler Room to FM Room	High	High	Gamma & H-3
9	Pressure Relief Duct to Soil	Regular	Low	H-3
10	Condenser Room to Soil	Regular	Moderate	None
11	Turbine Block	Regular	Moderate	None
12	Moderator Dump Tank to Soil	Regular	Moderate	High H-3

Primarily because of its use in reactor structures, concrete was classified as a critical component and a number of concrete cores were removed from various locations at NPD, Table 1, in early 1988.

Concrete is used in nuclear plants and associated facilities as:

(a) a containment boundary and biological shield,

(b) in nuclear waste repositories as engineered structural and backfill material,

(c) containers for irradiated fuel and other radioactive waste,

(d) a solidification matrix for low and intermediate level radioactive waste.

In view of the extensive use of concrete in nuclear facilities, the R&D program objectives relating to the NPD cores were expanded. Age and service related degradation effects in normal and high density concrete in nuclear service were to be determined as well as the radionuclide content and activity distribution in the various types of concrete exposed to neutron radiation and radioactive contamination. These data would provide valuable information on:

(a) the options available for the dismantling of concrete structures during the second phase of decommissioning ie 30 years post closure,

(b) the degree of radionuclide retardation provided by engineered concrete structures and cementitious backfill materials used in the construction of low and intermediate level radioactive waste disposal facilities, and

(c) the behaviour of tritium contamination in concrete structures associated with fusion reactor facilities.

This report describes a radiochemical characterization of the concrete cores removed from the shielding wall connecting the boiler room to the reactor vault identified as location No 2 and the wall forming the moderator dump tank sump, identified as Location 12 (Figure 1).

2.0 SAMPLES

2.1 Location 2

Four 15.25cm diameter through wall cores were obtained from location 2 identified/3/ as the wall between the boiler room and the reactor vault, Figure 2 Section A-A'. The concrete type is high density concrete (3692kg/m^3) containing Ilmenite-Hematite

ore. The composition is summarized in Table 2 /4/. Each of the four cores was removed from the wall in a number of smaller lengths, typically 20-30cms long.

TABLE 2

CHEMICAL COMPOSITION(%) OF NPD HIGH DENSITY CONCRETE

	CEMENT	AGGREGATE*
Loss on Ignition	1.8	-
SiO_2	21.1	3.7
Al_2O_3	5.0	3.1
Fe_2O_3	2.5	26.2
CaO	62.6	0.8
MgO	2.6	3.2
K_2O	0.96	-
Na_2O	0.21	0.3
SO_3	2.7	-
TiO_2	-	35
FeO	-	28.3
MnO	-	0.17
V_2O_5	-	0.3
Cr_2O_3	-	0.1
S	-	0.28
P_2O_5	-	0.015
Cu	-	0.02
Ni	-	0.03

* Typical chemical analysis of Ilmenite-Hematite ore. OHRD Report No. 56-551 Dec. 1956.

The cement aggregate ratio was 0.1 and the water cement ratio was 0.52. A small amount (0.2%) of lignin was also used to increase the residual water content of the heavy concrete. The elemental composition of the concrete is given in Table 3.

Figure 3(a) illustrates the numbering sequence for the sections from the boiler room to the reactor vault. For example 2B6 represents the section closest to the vault whereas 2B1 is the section closest to the boiler room.

2.2 Location 12

The second core sample characterized came from the moderator dump tank sump, Location 12, Figure 1. Regular density concrete was used in this structure and this location was chosen because of

TABLE 3

ELEMENTAL COMPOSITION OF NPD HIGH CONCRETE

Element	% by Weight
Hydrogen	0.24
Oxygen	34
Iron	36
Titanium	19
Silicon	2.4
Aluminum	1.9
Calcium	4.6
Magnesium	1.8

the presumed high levels of tritiated water vapour exposure in this area. Typical mix proportions of the concrete components for both ordinary concrete and high density concrete are given in Table 4 /5,6/.

TABLE 4

MIX PROPORTIONS FOR NPD NORMAL AND HIGH DENSITY CONCRETE

COMPONENT	NORMAL DENSITY		HIGH DENSITY	
	kg/m^3	%Vol	kg/m^3	%Vol
Sand	809	29	1361	30
Stone (Medium)	713	25	1885	41
Stone (Fine)	470	17	-	-
Cement	312	9	312	10
Water	183	17	165	16
Air	-	3	-	3

To minimize losses of tritium from the core sections, they were painted shortly after coring with a two component epoxy paint at NPD.

3.0 EXPERIMENTAL

The concrete sections were gamma scanned using an Aptec HPGe detector and a multichannel analyzer system made by Canberra. The counting time for the low activity sections was 5-20 hours and approximately 1 hour for the high activity sections.

The activity distribution in the cores as a function of distance from the vault was determined by drilling radially 3cm into the core and removing debris along the core section length using a

0.6cm drill bit. The sample, typically between 1.5 - 3 g, was gamma scanned for approximately 24 hours in the Biology Section low level laboratory and then leached with deionized water to extract the tritium. This method of sampling is not ideal because some tritium will escape due to frictional heat during the drilling. The prefered technique would have been to take larger subcores, therefore minimizing the amount of tritium lost but equipment was unavailable in the Radioactive Materials Laboratory to do this. We have assumed therefore that tritium is bound in hydrated cement and the degree of isotopic exchange with moisture in the air during the few minutes it takes to obtain a sample is negligibly small.

Carbon 14 in the samples was determined by heating the cement in a stream of moist air at 850-900^{o}C for 3 hours. Under these conditions the decomposition of all metal carbonates/bicarbonates to the corresponding oxides with liberation of CO_2 is expected to go to completion. The tritium in the moist air was removed in a gas bubbler acidified to pH<4. The moist gas, including $^{14}CO_2$ passed through this bubbler and was trapped in the second one containing Carbasorb, a solvent designed to remove CO_2 quantitatively. The C-14 in the Carbasorb was then determined by liquid scintillation counting.

A protocol to determine the concentration of the long lived isotopes, calcium-41 ($t_{1/2}$=8x10^{4}y) and nickel-63 ($t_{1/2}$=92y) in the cores from location 2 was developed by Analytical Services Section. The analyses are difficult because these isotopes decay by electron capture and by pure beta particle emission respectively and these processes are masked by more energetic decay schemes from other more abundant radionuclides such as Co-60, Cs-137, Eu-152/154 and tritium. The procedure/10/ therefore requires chemical separation of both calcium and nickel from each other and from other elements and then measuring the concentration of the active isotopes by liquid scintillation counting.

4.0 RESULTS AND DISCUSSION

4.1 NPD Reactor Design

In order to interpret the results of the core analyses it is necessary to understand the basic design of the NPD reactor. The calandria vessel is a horizontal cylindrical aluminum alloy vessel with double side and end walls (Figure 4). The inner vessel contains heavy water which acts as both the moderator as well as a neutron reflector. The annular gap of the vessel is filled with light water which acts as a secondary neutron reflector and a biological shield. The reactor vessel sits in an air ventilated concrete vault, lined on the inside with mild steel plate. The neutron losses from this design are greater than from Pickering and post Pickering Candu designs which have

substantially larger biological shields. As a consequence the vault concrete at NPD is expected to have been exposed to a significant neutron flux.

4.2 Radioactivity Associated With Cores From Location 2

4.2.1 Dose Rate Measurements

The activity levels on contact with the core sections were determined using a pancake detector and the values in Table 5 below represent the maximum levels recorded.

TABLE 5

NPD CORES FROM LOCATION 2

CORE ID	CORE SECTION LENGTH (cm)	ACTIVITY (cpm) SIDE	END
2A1		250	250
2A2		100	250
2A3		500	900
2A4		200	150
2B1	17	100	150
2B2	29	200	[illegible]
2B3	23.5	200	[illegible]
2B4	21.5	700	[illegible]
2B5	18	8000	[illegible]
2B6	19	60mR/h	125mR/h
2C1	23	100	100
2C2	27	4000	7000
2C3	26	200	200
2C4	28	200	100
2C5	26	35mR/h	125mR/h
2D1	26	150	100
2D2	30	250	200
2D3	30	2000	1800
2D4	21.5	10000	15000
2D5	21	40mR/h	55mR/h

4.2.2 Gamma Scanning

The high activity section of core 2A was not found in the shipment from NPD so very little work was done on this core. Measurements using a survey meter confirmed that the activity level increases towards the vault end of the core where neutron exposure and subsequent activation of the concrete is expected to

be significant. In situ gamma spectra of each section which would not differentiate between contributions from the cement and aggregate showed Co-60 as the predominant radioactive isotope contributing to the measured activity with Mn-54 present in smaller amounts in core sections 2A3 and 2C2.

When the cores were drilled to remove cement debris for analysis, the isotopes Mn-54, Co-60, Cs-134/137, Eu-152/154 and Ce-144 were identified with Co-60 being the predominant isotope. Table 6 summarizes the data which has been averaged for all the core sections analyzed from location 2.

TABLE 6

SPECIFIC ACTIVITY (Bq/g) IN HIGH DENSITY CONCRETE

ISOTOPE	VAULT END 0-24cm	B/R END 24-130cm
H-3 ($t_{1/2}$=12.3a)	674	4625
C-14 ($t_{1/2}$=5730a)	16	296*
Ca-41 ($t_{1/2}$=80000a)	<2	not measured
Mn-54 ($t_{1/2}$=303d)	34	<1
Co-60 ($t_{1/2}$=5.3a)	1770	9
Ni-63 ($t_{1/2}$=92a)	3	not measured
Cs-137 ($t_{1/2}$=30.2a)	4	<1
Cs-134 ($t_{1/2}$=2.1a)	6	<1
Ce-144 ($t_{1/2}$=284d)	11	<4
Eu-152 ($t_{1/2}$=13a)	51	<1
Eu-154 ($t_{1/2}$=16a)	7	<1

* One analysis only, taken from the surface of the boiler room side of the core section.

The activity of Co-60 in the cement at the vault end of the cores was three orders of magnitude greater than at the boiler room end. The same trend was apparent for the other gamma emitting isotopes, but the effect is less pronounced because their specific activities are so small.

As Figure 5 illustrates, the activity of Co-60 decreased rapidly with distance into the core and within 30 cms of the vault end the activity of Co-60 was less than 10 Bq/g. The chemical analysis of the cement debris for inactive cobalt (Co-59) gave a concentration of 47±11 mg/kg which is somewhat higher than the cobalt concentration given in reference 5 (23mg/kg). From the axial thermal neutron flux data and NPD power history from reference 5 it is possible to calculate the expected Co-60 concentration per gram of concrete using equation 1/6/.

$$A = \phi.\sigma.N(1-e^{-(0.693.t/t1/2)})\text{--------}(1)$$

where A = specific activity of isotope produced by activation (Bq/g)
ϕ = neutron flux (neutrons.$cm^{-2}.s^{-1}$)
σ = neutron capture cross section (cm^2) of atom to be activated
N = Number of atoms available to be activated/g concrete
t = neutron exposure time
t1/2 = half life of radioactive isotope produced.

Using the average concrete flux of 5 x 10^8 n.$cm^{-2}.s^{-1}$ over a 20cm thickness of concrete/7/, a Co-59 neutron absorption cross section of 19 barns, and an irradiation time of 16 years at full power, the specific activity of Co-60 produced is calculated to be 4000 Bq/g which is within a factor of 2 of the average measured value at the vault end of the core. As Table 3 shows, iron makes up 36% of the weight of the concrete from this location. Iron-55, the neutron activation product of stable Fe-54 is expected to be present in significant amounts in the concrete at the vault end of the cores. This isotope has a 2.6y half life and is an X-ray emitter. Consequently it is a difficult isotope to detect in a high density matrix such as concrete and in the presence of other gamma emitters. Given this difficulty and the fact that Fe-55 is a short lived, low energy emitter we have not tried to determine its concentration in concrete. However in view of the good agreement between the measured and calculated Co-60 values, a similar calculation for Fe-55 gives a specific activity of 323kBq/g. This isotope is therefore the most abundant neutron activation product in high density concrete in agreement with previous calculations/7/.

Samples of the steel rebar were removed from core sections 2B6 and 2D5 both located close to the vault end. Only the isotopes Co-60 and Mn-54 were observed in the gamma spectra, Table 7.

The cobalt content of the rebar was not specifically determined but it was assumed that it would be similar to that of the cement/aggregate mix. The very low levels of activity therefore confirm the rapid attenuation of the neutron flux in the cores observed in the Co-60 distribution in the cement.

TABLE 7

SPECIFIC ACTIVITY (Bq/g) OF Co-60 AND Mn-54 IN REBAR

Location	Co-60	Mn-54
2B6	63	4
2D5	41	2

4.2.3 Calcium-41 and Nickel-63 Determination

Table 8 summarizes the results of the Ca-41 and Ni-63 determinations. The uncertainties in the data are due essentially to counting statistics and do not represent the reproducibility of the measurements.

TABLE 8

SPECIFIC ACTIVITY (Bq/g) OF Ca-41 AND Ni-63 IN CORE DEBRIS

SAMPLE	DIST.FROM VAULT END(cm)	NICKEL-63	CALCIUM-41	COBALT-60
2B6-1	1.3	1.4±0.3	<0.7	2862
2C5-1	2.5	0.5±0.2	<0.5	3071
2C5-2	7.6	2.7±0.5	<0.5	1720
2D5-1	1.9	6.0±0.5	0.9±0.4	2235

The Co-60 activity of the samples is also shown for comparison. The smaller Co-60 activity in sample 2C5-2 compared to 2C5-1 is due to neutron flux attenuation and this trend, observed also for Eu-152/154 and Mn-54 is also expected to be observed for the Ni-63 and Ca-41 isotopes since these too are formed in situ by neutron activation. However this was not found to be the case. On the contrary, the concentration of Ni-63 was apparently higher in the sample exposed to a lower flux. The most likely explanation for this is that the amount of sample used in these determinations was small and with the complex protocol to extract nickel and calcium chemically there was large uncertainty in the quantity of these elements in the original samples. Future analyses should be carried out on larger amounts of sample. Calculations based on the nickel and calcium content of the concrete (Tables 1 and 2) suggest an estimated Ni-63 and Ca-41 content of 95 and <1 Bq/g respectively.

4.2.4 Carbon-14

The C-14 analyses of core section 2C showed that C-14 concentrates at the surface of the boiler room end of the core. The activity at this location (296 Bq/g) was 4 times the concentration measured at the vault end (67Bq/g). The activity decreased to background levels (4Bq/g) within 0.5 cm of vault surface. Because of these low levels the C-14 distribution at the boiler room end were not investigated further. The lower concentration of vault C-14 compared with boiler room C-14 is not a surprising observation since the mild steel liner on the inner vault wall is expected to prevent access of $^{14}CO_2$ (produced by neutron activation of nitrogen-14 in air) to the concrete surface at the vault end. The small quantity of C-14 detected at the vault end can come from four sources:

(a) activation of nitrogen in the concrete $^{14}N(n,p)^{14}C$,

(b) activation of oxygen in concrete $^{17}O(n,alpha)^{14}C$,

(c) activation of carbon in concrete, $^{13}C(n,gamma)^{14}C$ and

(d) contamination.

Of the neutron activation pathways, (b) is the most likely in view of the large concentration of oxygen in concrete relative to nitrogen and carbon but calculations indicate an expected specific activity from this source to be of the order of only 1Bq/g, less than the minimum detectable level and considerably less than found. We therefore attribute the C-14 at the vault ends of the concrete cores to be due to contamination from the boiler room ends where the levels are higher. The C-14 found here likely has its origins from moderator or HT water containing dissolved $^{14}CO_2$ as bicarbonate or carbonate which becomes airborne by exchange with $^{12}CO_2$ in the air.

4.2.5 Tritium

The distribution of tritium as tritiated water in cores 2B, 2C and 2D is similar. Figure 6 shows the distribution for core section 2B. The lower concentration of tritium at the vault end (300-500 Bq/g) relative to the boiler room end is attributed to the protective steel plate preventing water vapour access to the concrete. There is a maximum tritium activity of 12-15 kBq/g which occurs approximately 5 cm from the boiler room end of each core. This is expected and is the consequence of tritium loss from the core end during the drilling operation and subsequent handling. By measuring the area under the curve in Figure 6 and using a concrete density of 3.69g/cm^3, the total tritium in core section 2B1 is calculated to be 107.4MBq (2.9mCi). This represents 56% of the total tritium (192MBq) in the entire core

distributed over only 11cm or 8% of the 130cm length of the core. This calculation assumes that (a) the tritium in the concrete is associated with all of the components of the concrete and (b) the drilling debris analysed for tritium is representative in composition of the entire core. This assumption is necessary because the aggregate in high density concrete is quite small and is composed of relatively soft iron ore which has hydrated forms.

4.3 RADIOACTIVITY ASSOCIATED WITH CORES FROM LOCATION 12

The core from this location had a total length of 135cm and was removed in six sections. The numbering designation is shown in Figure 3(b). The activity of the gamma emitting radionuclides Co-60, Cs-137/134 was determined to be less than 5Bq/g but the maximum tritium activity was 82kBq/g compared to 15kBq/g at location 2. The total tritium inventory in core section 12C-1 was determined to be 558MBq (15mCi) by measuring the area under the tritium distribution curve in Figure 7 and using a density of 2.49g/cm^3 for regular density concrete. This calculation overestimates the total tritium inventory because the drill debris contains no aggregate (unlike high density concrete) but mostly hydrated cement and sand in which most if not all of the tritium resides. If this point, that tritium is only associated with 52% of the mass of concrete is factored into the calculation, the revised tritium inventory in core section 12C-1 is only 290MBq (7.8mCi).

4.4 BEHAVIOUR OF TRITIUM IN HIGH AND REGULAR DENSITY CONCRETE

The tritium diffusion rates into 150 mL/min dry flowing air from the boiler room end of core section 2B1 and 12C1 were measured over a period of nearly 5 months. The experiment was carried out so that only the tritiated water flux from the flat face of the core (182.4cm^2) was determined. The cumulative fraction of tritium released (CFR) from the cores will be dependent on both the surface area and the volume of the core sections. The volume is in effect representative of the tritium concentration in the core. Therefore to compare the tritium desorption rates from the two core sections which are of different size, the cumulative fraction released is normalized by dividing it by the ratio of S/V where S is the surface area across which tritium is allowed to diffuse and V is the volume of the core. This normalized CFR is plotted for high and regular density concrete as a function of time in Figure 8.

There is initially a more rapid release of tritium from both core surfaces in the first 20 days followed by a steady desorption rate of 5.0×10^{-3} cm.day^{-1} and 1.5×10^{-3}cm.day^{-1} for regular and high density concrete respectively. This is similar to the washout effect observed in normal leaching experiments where in the initial period, surface enriched contamination is rapidly

washed off the surface. The data suggests that the pore volume for high density concrete is about a factor of three lower than in regular density concrete.

4.5 MODELING OF TRITIUM DESORPTION DATA

To describe the release of radioactivity from waste, several workers have employed a semi-infinite plane source diffusion model based on mass transport theory/11,12/. Diffusion of a stable isotope from a homogenous, planar semi-infinite medium having a surface concentration of zero for t > 0 is given by

$$\frac{\Sigma a_n}{A_o} \cdot \frac{V}{S} = 2\,(D_e/\pi)^{1/2} \cdot (\Sigma t_n)^{1/2} \quad \text{-------(2)-------}$$

where Σa_n = cumulative release of radioactivity
A_o = initial inventory of radioactive isotope in waste
V = specimen volume (cm^3)
S = exposed surface area of specimen (cm^2)
D_e = effective diffusivity of isotope ($cm^2.s^{-1}$)
Σt_n = cumulative time (s)

A plot of the cumulative fraction released against the square root of time should produce a straight line graph going through the origin. Figures 9 and 10 show a small deviation from this for both of the core sections investigated. The intercept at t=0 is negative which is indicative of a delay or lag in the tritium reaching the surface prior to desorption. This is consistent with our observation that the surface of the cores is slightly depleted in tritium relative to the adjacent inner layer.

The effective diffusivity, D_e, calculated from the gradients of the lines for high and regular density concrete is $5.2\times10^{-9} cm^2.s^{-1}$ and $6.6\times10^{-8} cm^2.s^{-1}$ respectively. This difference in D_e reflects the lower porosity of high density concrete. These results are in good agreement with published data/13/, ($6.7\times10^{-9} cm^2.s^{-1}$) and a recent determination of the diffusion of tritium in uncarbonated and carbonated cement at OHRD/14/, which gave diffusivities of 1.4×10^{-8} $cm^2.s^{-1}$ and $0.6\times10^{-8} cm^2.s^{-1}$ respectively. By way of comparison, the diffusivity of tritiated water in light water, also called the self diffusion coefficient is of the order of 10^{-4} $cm^2.s^{-1}$. Incorporation of tritiated water in concrete therefore provides a retardation factor of 4 orders of magnitude/14/. The good agreement between the NPD concrete data and cement data validates the earlier assumption that tritium in the NPD concretes is associated exclusively with the cement paste in the concrete.

5.0 SUMMARY AND CONCLUSIONS

The inventory and axial distribution of radionuclides in high and regular density concrete removed from NPD NGS have been

determined. The high radiation field on contact with the vault ends of the high density cores is due to Co-60 which has a specific activity of 1800 Bq/g when averaged over a distance of 20 cm from the reactor vault end. Beyond 20cm into the core the neutron flux attenuation is such that the Co-60 specific activity is <50 Bq/g.

Other gamma emitting radionuclides present in high density concrete are Mn-54, Cs-134/137, Eu-152/154 and Ce-144 but the specific activity of these is <35 Bq/g.

With the exception of tritium, all radionuclides in regular density concrete removed from the moderator dump tank sump wall have specific activities less than 5 Bq/g. The tritium specific activity varies along the length of the core section but its maximum activity is 82 kBq/g. This is five times the maximum tritium activity found in high density concrete(15kBq/g).

Under the conservative experimental conditions (flowing dry air), the tritiated water diffuses out of regular density concrete about 3 times faster ($5x10^{-3}$ cm/day) than from high density concrete ($1.5x10^{-3}cm.day^{-1}$). The effective diffusivity, D_e, of tritiated water for high and regular density concrete is $5.2x10^{-9}cm^2.s^{-1}$ and $6.6x10^{-8}cm^2.s^{-1}$ respectively.

Of the pure beta emitters C-14, Ca-41 and Ni-63, C-14 is the more abundant but its specific activity is low <300Bq/g. The specific activity of Fe-55 a low energy X-ray emitter was not determined directly due to the difficulty of the analysis but its calculated maximum concentration is 323kBq/g which would make it the most abundant radioisotope in high density concrete. However its low energy radiation and its relatively short half life (2.6y) makes Fe-55 a relatively unimportant isotope with respect to Phase II decommissioning and subsequent waste management strategies.

The information generated in this report will provide a guide in the development of decontamination and waste management strategies when planning Phase II decommissioning. For example at the end of the 30 year Phase I of decommissioning, the activity of the concrete from NPD will be dominated by tritium. Decontamination of the concrete could be achieved for example by providing suitably sized air purge flow through the boiler room 5 years or so before starting Phase II decommissioning. This would promote the diffusion of tritium from concrete, reduce the chronic airborne tritium hazards during Phase II decommissioning and result in a large volume of radioactive waste that could be effectively declared de minimis or below regulatory concern after decontamination. In addition the tritium diffusion data allows an assessment of the radiation hazards due to tritium and the mitigating techniques required to protect workers during Phase II decommissioning activities.

6.0 RECOMMENDATIONS

The analysis of NPD cores described in this report is the first attempt to characterize concrete exposed to a variety of radiation sources. The knowledge on which to base waste management or health and safety associated decisions is therefore very limited. It is recommended that concrete specimens removed from Candu reactors for example from Douglas Point or Pickering be archived for later characterization studies.

The work reported here determined the behaviour of tritiated water in concrete. This is certainly the most significant problem associated with concrete waste produced during the decommissioning of CANDU nuclear plants. At the Darlington Tritium Removal Facility large quantities of tritiated water and elemental tritium will be handled. Tritium gas by virtue of its high mobility is expected to penetrate to a greater degree than tritiated water. Competing reactions such as oxidation to water or radiolytically catalyzed tritiation of organics in the concrete such as superplasticizers may give rise to a complex mixture of tritiated species whose behaviour is unknown. Some effort therefore should be invested in determining the behaviour of tritium gas in concrete.

7.0 ACKNOWLEDGEMENT

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Approved by:

D.J.R. Dodd
Manager
Chemical Research Department

Prepared by:

J.P. Krasznai
Research Scientist
Materials Chemistry Section

Reviewed by:

R.W. Glass
Supervising Chemist
Materials Research Section

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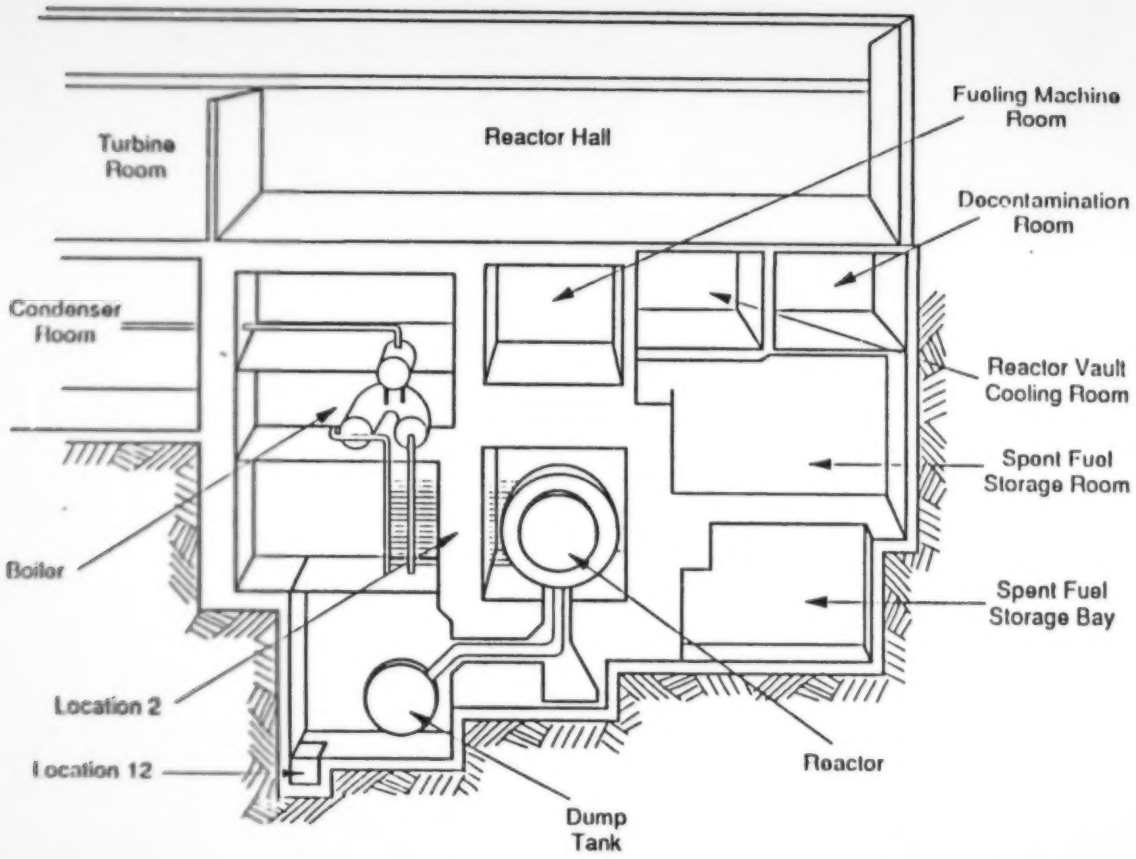
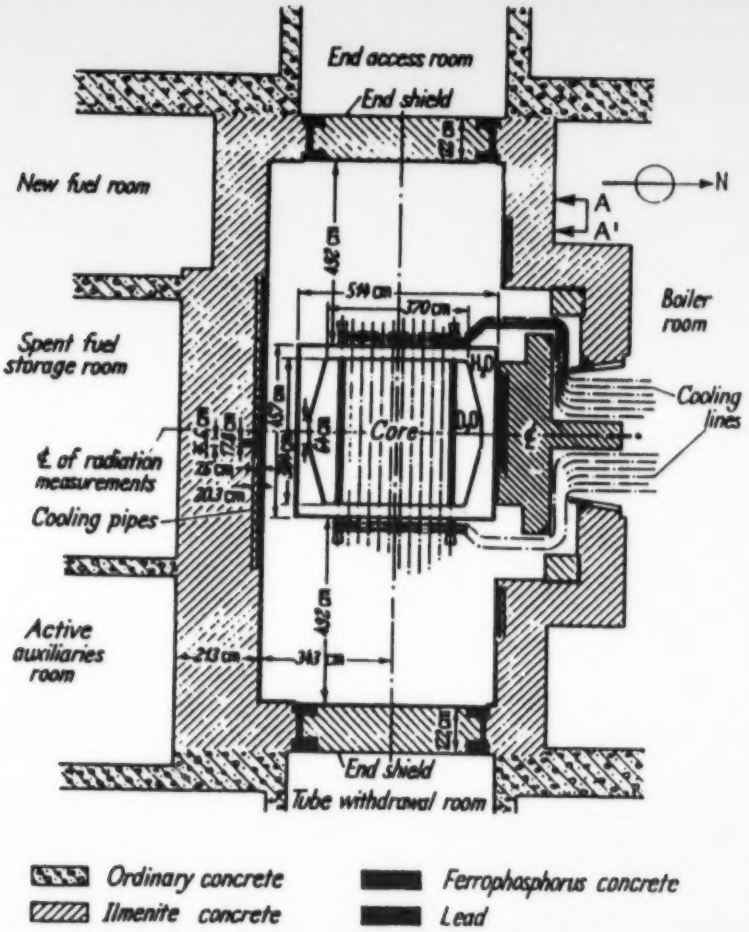


FIGURE 1

Origin of High Density Concrete Samples(2) and Regular Density Concrete Samples(12)



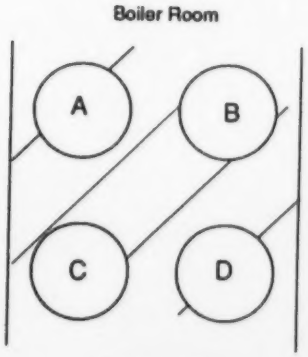


FIGURE 2

LOCATION 2 CORES

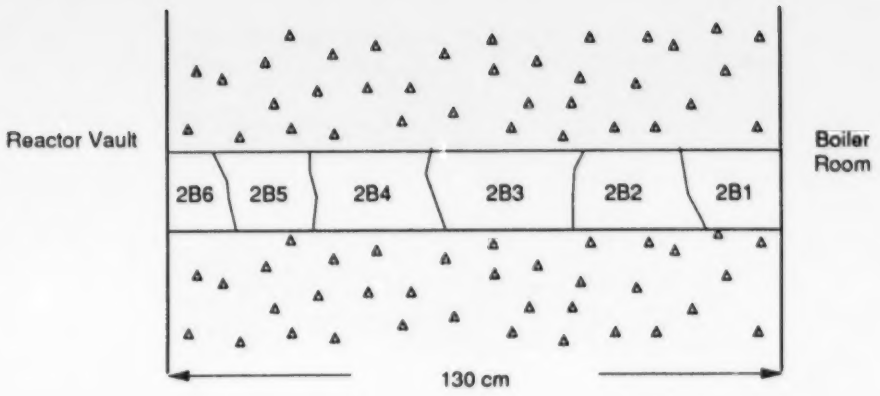


FIGURE 3(a)

TYPICAL AXIAL VIEW OF LOCATION 2 CORES

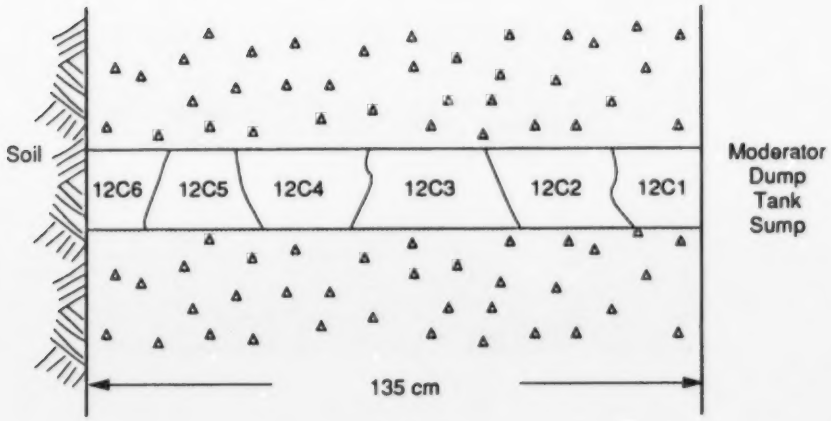


FIGURE 3(b)

AXIAL VIEW OF LOCATION 12 CORES

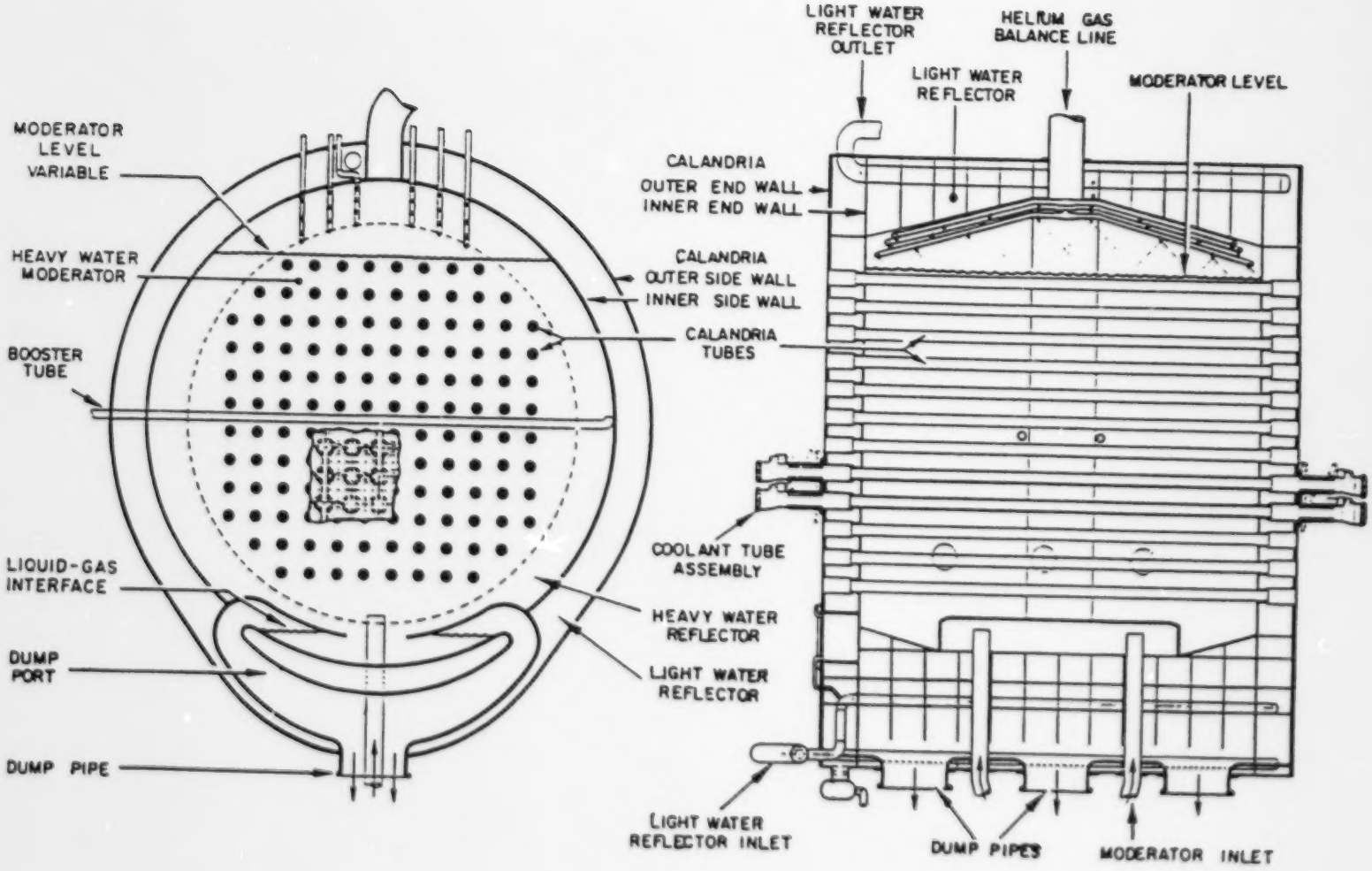


FIGURE 4

N P D-2 REACTOR ARRANGEMENT

90-285

188008-RD

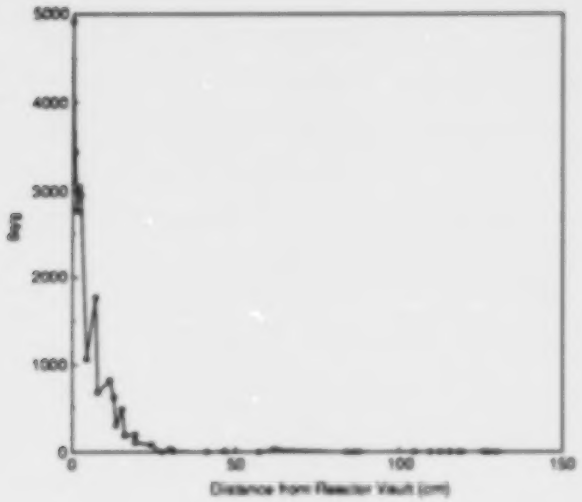


FIGURE 5

COBALT-60 DISTRIBUTION IN HIGH DENSITY CONCRETE

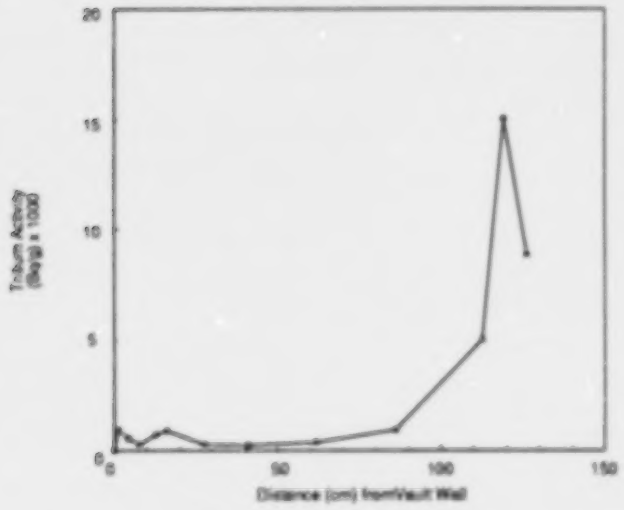


FIGURE 6

TRITIUM (HTO) DISTRIBUTION IN HIGH DENSITY CONCRETE
(CORE 2B)

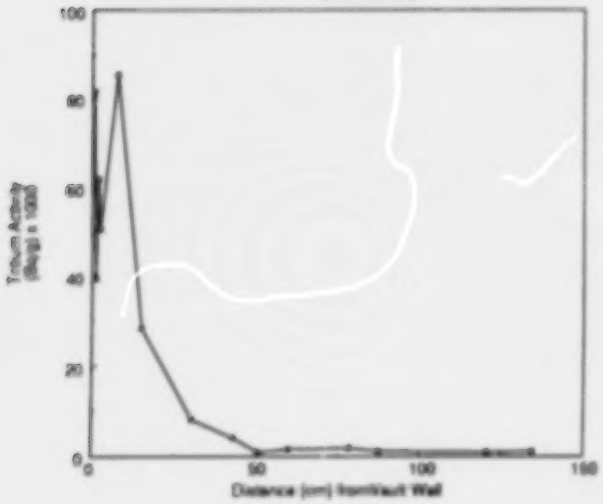


FIGURE 7

TRITIUM (HTO) DISTRIBUTION IN NORMAL DENSITY CONCRETE
(CORE 12C)

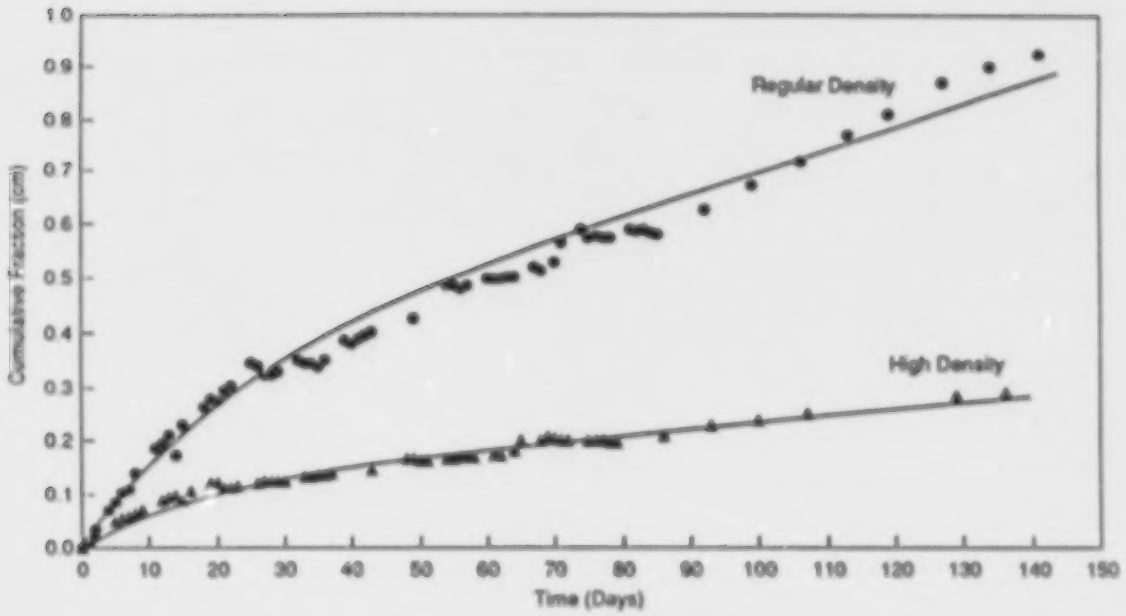


FIGURE 8

TRITIUM RELEASED AS A FUNCTION OF TIME
FROM REGULAR AND HIGH DENSITY CONCRETE

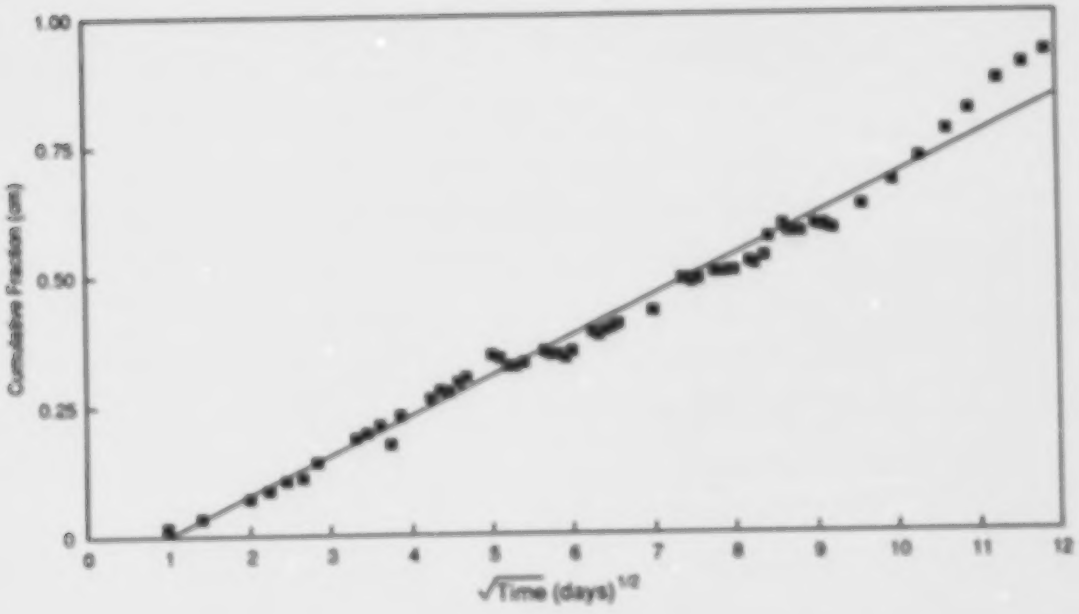


FIGURE 9

TRITIUM RELEASED FROM REGULAR DENSITY CONCRETE

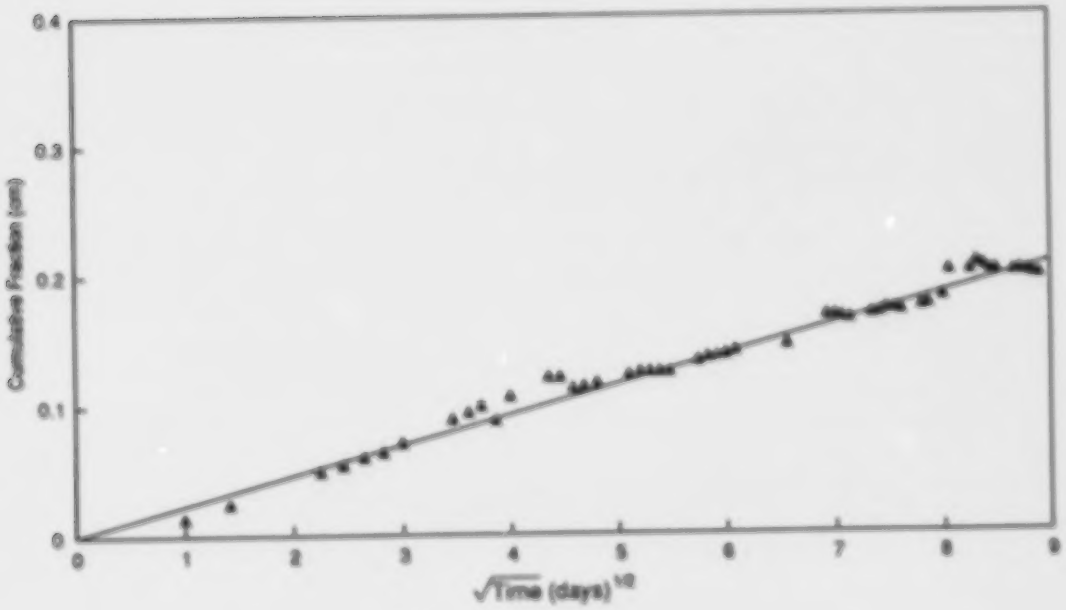


FIGURE 10

TRITIUM RELEASED FROM HIGH DENSITY CONCRETE